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# Development of an Infrared Fluorescent Gas Analyzer

Akron Scientific Laboratory

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A prototype model low level carbon monoxide analyzer was developed using fluorescent cell and negative chopping techniques to achieve a device superior to state of art NDIR analyzers in stability and cross-sensitivity to other gaseous species. It is clear that this type of analyzer has that capacity. More effort will have to be devoted to an investigation of the effects of ambient temperature and pressure variation on the span and zero stability of the fluorescent CO analyzer before its true performance advantages can be assessed. The prototype analyzer, which is a self-contained unit powered from 115V 60 HZ line, showed an ultimate detectivity to CO of approximately 1 ppm, and no measurable cross sensitivity to any other gaseous species at the level normally found in the ambient atmosphere.

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# DEVELOPMENT OF AN INFRARED FLUORESCENT GAS ANALYZER

By

E.A. McClatchie

ARFR-14

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TABLE OF CONTENTS


| | | Page |
|---|---|---|
| 1. | INTRODUCTION | 1 |
| 2. | THEORY OF OPERATION | 1 |
| 3. | RESULTS TAKEN WITH THE PROTOTYPE ANALYZER | 4 |
| 4. | CONCLUSIONS | 7 |

## 1. INTRODUCTION

This report covers the work performed by Arkon Scientific Labs under Contract CPA-70-152 to the National Air Pollution Control Administration (NAPCA).

The aim of this contract was to develop a prototype model low level carbon monoxide analyzer using the Arkon Scientific Labs fluorescent cell and negative chopping techniques to achieve a device superior to state of the art NDIR analyzers in stability and cross-sensitivity to other gaseous species.

The prototype analyzer, a completely selfcontained unit powered from 115 V 60 HZ line, was delivered to NAPCA in January 1971. It showed an ultimate detectivity to CO of approximately 1 ppm, and no measurable cross-sensitivity to any other gaseous species at the level normally found in the ambient atmosphere.

## 2. THEORY OF OPERATION

The analyzer uses the principle of infrared fluorescence, where a vibrationally excited molecular species decays electromagnetically and emits a line spectrum of infrared radiation which is an exact match of the infrared absorption spectrum of that molecule. Two isotopic forms of carbon monoxide are used in the fluorescent mode. One, the normally abundant species $CO^{16}$, was used to provide the measuring beam of the instrument since $CO^{16}$ fluorescent radiation is strongly absorbed by normal carbon monoxide. The second beam, $CO^{18}$ fluorescent radiation, was used to provide a reference beam since the variety of radiation is only weakly absorbed by the low abundance of this isotope of carbon monoxide in nature.

Referring to Figure 1, the operating principles of the instrument are as follows:

Infrared radiation from the black body source is used to vibrationally excite the carbon monoxide molecules in a sealed fluorescent cell. The fluorescent cell contains a mixture of two isotopes of carbon monoxide at pressures of approximately 8.0 torr each and is filled to 1 atmosphere total pressure with Argon as a buffer infrared neutral gas. The gases in the cell are of extremely high purity so that the vibrationally-excited molecules de-excite by re-emission of electromagnetic radiation; i.e., fluorescent radiation. Thus, the cell continuously emits both $CO^{16}$ and

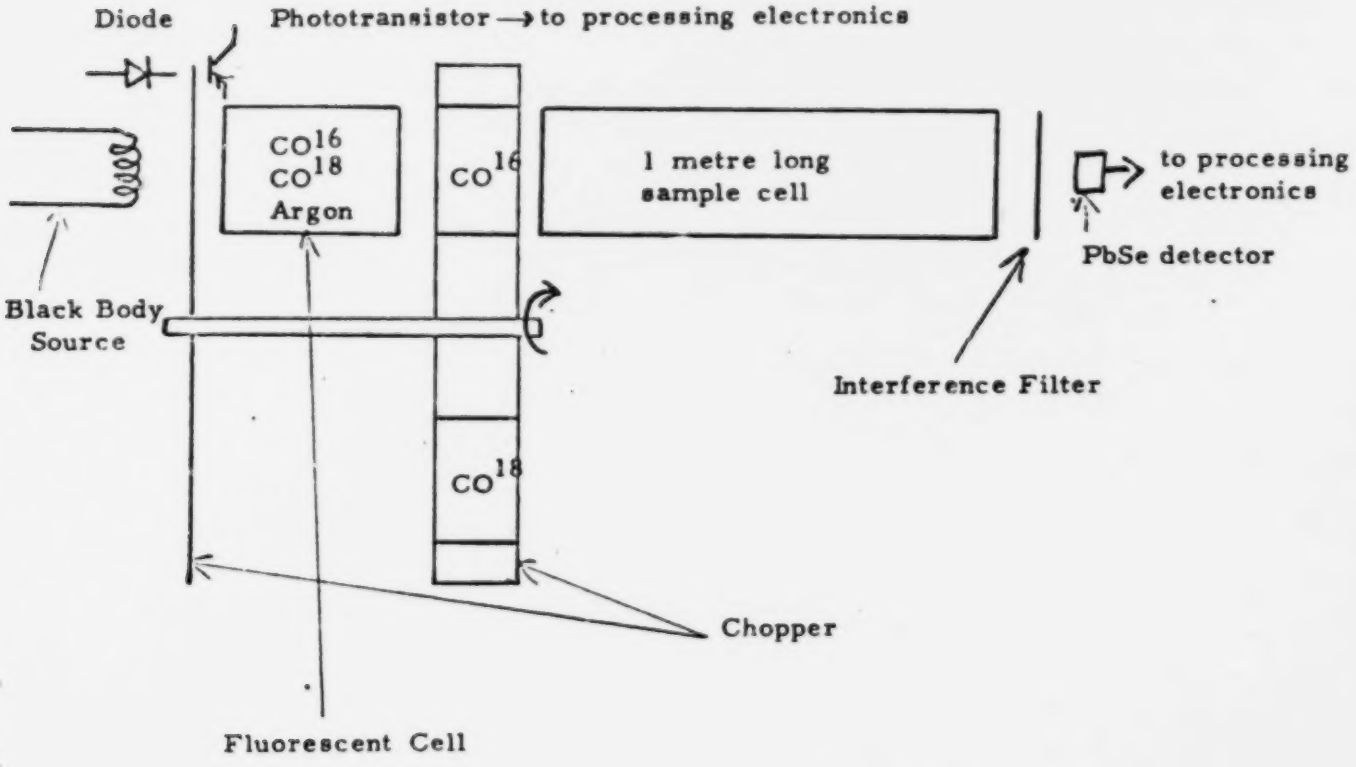


Figure 1. Arkon 0-20 ppm Carbon Monoxide Analyzer

and $CO^{18}$ fluorescent radiation. The emitted radiation is chopped by negative chopper cells containing $CO^{16}$ and $CO^{18}$ alternately. The negative chopper cells contain impure carbon monoxide so that they absorb the appropriate variety of fluorescent radiation. The complete chopper consists, as shown in Figure 1, of two blades rotating on a common shaft. When rotated, the fluorescent cell is alternately exposed to exciting radiation from the black body source and then allowed to shine its fluorescent radiation through a negative chopper cell and sample tube to the detector.

Thus the infrared detector receives alternate pulses of $CO^{16}$ and $CO^{18}$ fluorescent radiation which have passed through the gas sample to be measured. Referring to Figure 2, if the $CO^{16}$ and $CO^{18}$

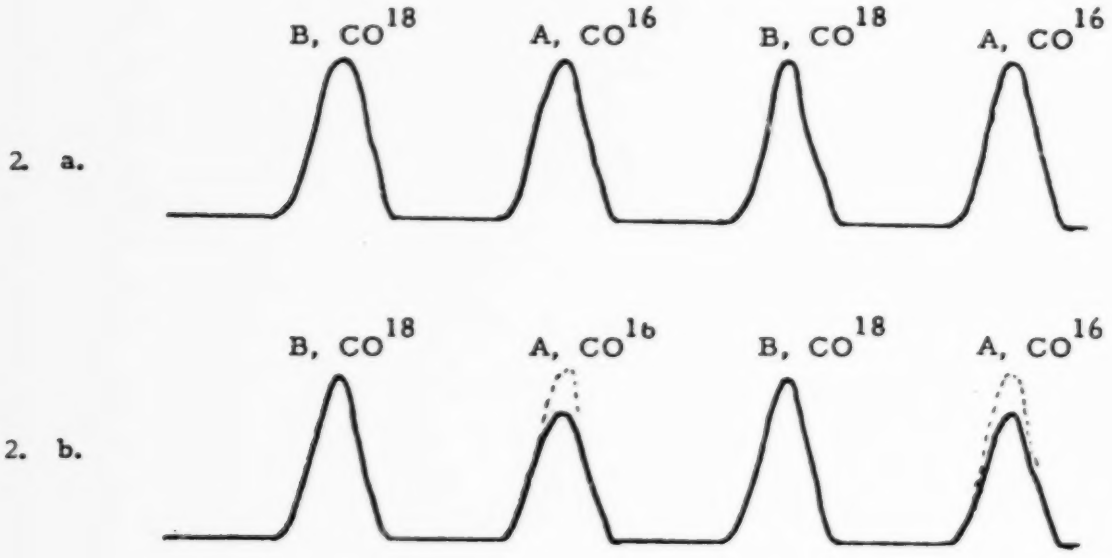


Fig. 2. a. Detector signals with no CO in sample tube
b. Detector signals with CO in sample tube

signals are defined as the "A" and "B" signals, then since the natural isotopic abundance of $CO^{18}$ is only 0.2% of $CO^{16}$, only the "A" signal will be attenuated by the presence of CO gas in the analyzer sample tube. A light emitting diode and phototransistor on the chopper wheel (see Figure 1) provide logic signals to the electronics for identification of the A and B pulses. The A and B pulses are then routed into separate demodulators where they are synchronously demodulated and smoothed. In addition, an automatic gain control circuit maintains the "B" signals at fixed amplitude regardless of variations of source power or detector response. The processing electronics then generates an output proportional to the quantity

$$\frac{B - A}{B}$$

and this expression should only be sensitive to differential absorption of the A and B signals which to first order can only occur due to the presence of carbon monoxide in the sample tube.

## 3. RESULTS TAKEN WITH THE PROTOTYPE ANALYZER

Part of a chart recorder trace of the analyzer output is shown below in Figure 3. In this case the analyzer was set up for 50 ppm CO full scale and the chart recorder trace shows the variation of CO level over a two mile run through the downtown section of Berkeley, California, near our plant. The analyzer is obviously capable of accurately measuring CO concentration in the 0-50 ppm range.

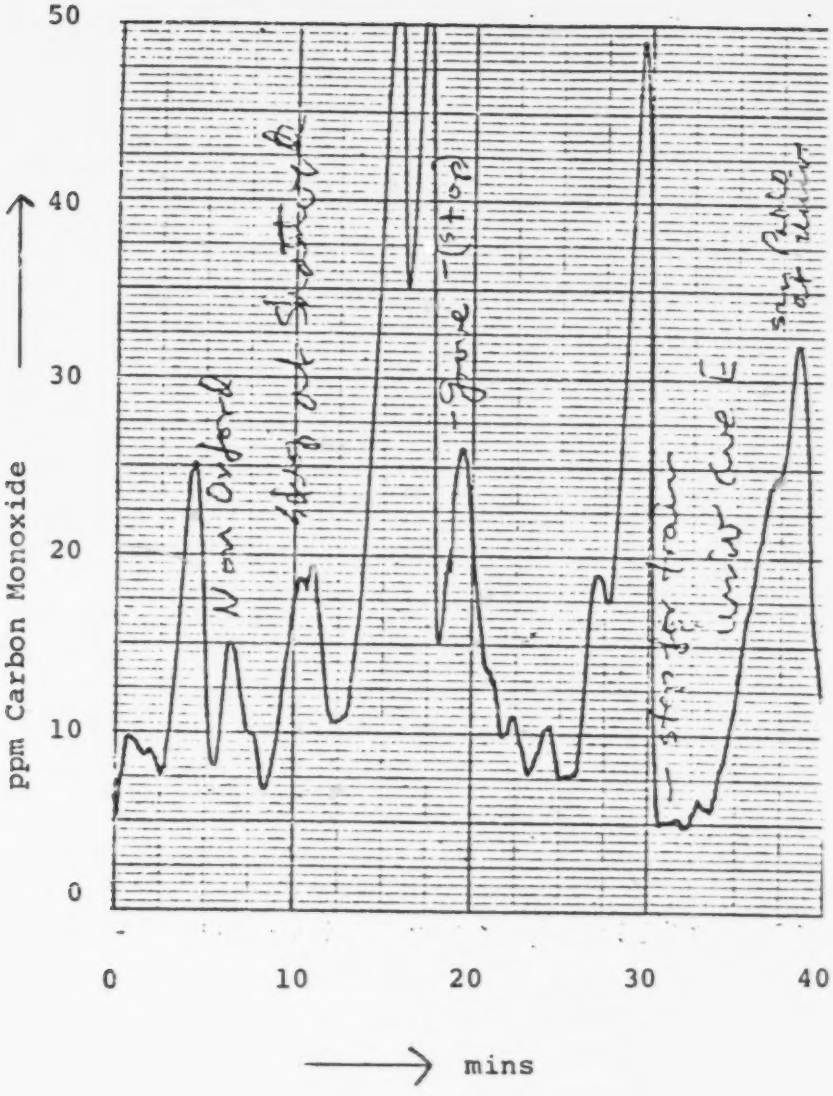


Figure 3. Carbon monoxide distribution in downtown Berkeley, California, streets

Under constant temperature laboratory conditions, a series of carbon monoxide readings taken every 10 seconds over a period of 5 minutes showed a variation from a highest recorded value of 50.5 to a lowest value of 46.0 with nominal 49 ppm CO span gas flowing through the instrument. A root mean square analysis of the 30 recorded readings showed that the R.M.S. noise of the analyzer was 0.7 ppm CO.

Possible cross-sensitivities of the prototype analyzer to other gases were investigated specifically for the gases $CO_2$, $CH_4$ and $H_2O$. For 100% $CO_2$ the analyzer showed a downscale reading of - 25 to 30 ppm CO, or a rejection ratio of - 30,000:1. For 100% $CH_4$ and saturated $H_2O$ vapor at room temperature (approximately 1%) the instrument showed no deflection within its noise limit.

The performance of the prototype analyzer can therefore be summarized as follows:

| | | |
|---|---|---|
| Minimum detectable value of CO: | | 0.7 ppm |
| Rejection ratio to other gases - | $CO_2$: | 30,000:1 |
| | $H_2O$: | > 10,000:1 |
| | $CH_4$: | > $10^6$:1 |

Only limited temperature coefficient data was obtained with the prototype analyzer. The measured zero drift was of the order of 5 - 10 ppm CO per °C change in ambient temperature. It was identified that the major contributor to this drift was the change in temperature of the infrared detector. The temperature change in the detector element caused a differential change in its response to $CO^{16}$ and $CO^{18}$ fluorescent radiation and hence a severe zero drift in the analyzer.

## 4. CONCLUSIONS

A prototype carbon monoxide analyzer using an infrared fluorescent source has been built and undergone a preliminary testing program. It is clear that this type of analyzer has the capability to advance the state of the art in NDIR carbon monoxide measurement devices in the areas of stability and freedom from interferences by other gases. More effort will have to be devoted to an investigation of the effects of ambient temperature and pressure variation on the span and zero stability of the fluorescent CO analyzer before its true performance advantages can be assessed. A potential factor of 10 improvement in CO noise level would be attainable by a thorough upgrading of the optical components of the analyzer.